MATERIALS BENCHMARKING ACTIVITIES FOR CAMP FACILITY

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Argonne NATIONAL LABORATORY

Project ID: BAT028

OVERVIEW

Timeline
- Start – Oct. 1st, 2014
- Finish – Sep. 30th, 2023

Budget
- Total project funding in FY2022: $400K (as part of CAMP effort)
- 100% DOE

Barriers
- Development of sustainable EV batteries that meet or exceed DOE/USABC goals
  - Cost
  - Performance
- High energy active material identification and evaluation

Partners and Collaborators
- Coordinated effort with DOE-EERE-VTO BTMS, Silicon Consortium Project (SCP), Realizing Next Generation Cathodes (RNGC), ReCell, XCEL Phase II
- INL, LBNL, NREL, ORNL, PNNL, SLAC, SNL
- Argonne Facilities: APS, CNM, EADL, MERF, PTF
- See collaboration list in separate slide

RELEVANCE

- An overwhelming number of materials are being marketed/reported to improve Lithium-ion batteries, which need to be validated for their impact on EV applications.
- CAMP Facility was established at Argonne to provide a realistic and consistent evaluation of candidate materials. Cell materials need to be validated internally to determine if they warrant further consideration.
- The benchmarking (validation) activities can also provide an objective opinion to material developers. Moreover, the better understanding of the active materials at cell level will speed up material development efforts.

FY22 MILESTONES AND ACCOMPLISHMENTS

Milestone	Planned End Date	Type	Status
Develop methods to coat electrode-ceramic structures using reverse comma coating methods. **(see BAT030)** ➢ Produce 10 meter of electrode-ceramic on foil with at least 3 mAh/cm² loading.	7/30/2021	Quarterly Progress	Completed
Develop methods to coat electrodes with novel solid-state electrolyte materials that are being developed in literature. **(see BAT030)** ➢ Produce 5 meters of cathode electrode with solid-state electrolyte.	7/31/2022	Quarterly Progress	On Schedule

COVID-19 reduced lab time and may cause delays in completing FY22 milestones

Accomplishments
- Various solid electrolytes were explored and studied
  - PEGDA solid polymer electrolyte preparation and electrochemical characterization
  - Li_6PS_5Cl solid electrolyte was tested in all solid-state battery development using Si as anode and NM811 as cathode
  - Solid state electrolyte optimization via X-ray imaging
  - Lithium dendrite formation and propagation in solid-state electrolyte was investigated using an electrochemical-mechanical model
- Electrochemical performance characterization of sulfur-carbon material from Zeta Energy.
- Carbon Nano Structure materials from Cabot as conductive additive for lithium-ion battery

APPROACH AND STRATEGY

- Collaborate with material developers and leverage Argonne's expertise in electrode design and cell testing.
- Cell materials that have an impact on the cell performance will be considered for testing, mainly in terms of:
  - Electrochemical performance
  - Electrode optimization
  - Thermal stability
- The electrochemical performance will be validated using 2032 coin type cells under test protocol derived from USABC EV requirements.

United States Advanced Battery Consortium Battery Test Manual For Electric Vehicles, U.S. Department of Energy Vehicle Technologies Program, Revision 3.1, October 2020

USABC Requirements of Energy Storage Systems for EV

Characteristics at EOL (30°C)	Unit	Cell level
Peak discharge Power Density (30 Sec)	W/L	1500
Peak Specific discharge Power (30 Sec)	W/kg	700
Peak Specific Regen Power (10 sec)	W/kg	300
Available Energy Density @ C/3 discharge rate	Wh/L	750

Test Protocol development

Electrochemical test protocol, such as formation, C-rate and cycle life, were established for half and full cells according to EV requirements.

OBJECTIVES

- To identify and evaluate sustainable low-cost cell chemistries that can simultaneously meet the following criteria for EV applications:
  - Electrochemical performance
  - Abuse tolerance
  - Cost
- To enhance the understanding of advanced cell components on the electrochemical performance and safety of LIB.
- To support the CAMP Facility for prototyping cells and electrode library development.

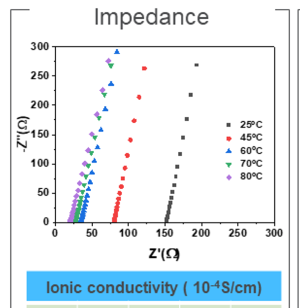
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

SOLID POLYMER ELECTROLYTE (SPE) PREPARATION AND CHARACTERIZATION

- Solid polymer electrolyte (SPE) was prepared using poly (ethylene glycol) diacrylate (PEGDA) as a cross-linking agent to copolymerize with other monomers.
- Instead of UV curing, PEGDA based SPE were enabled through an in-situ **thermal polymerization method**.

Weight %			
PEGDA	LiTFSI	GN	AIBN
40	30	30	0.1

Impedance

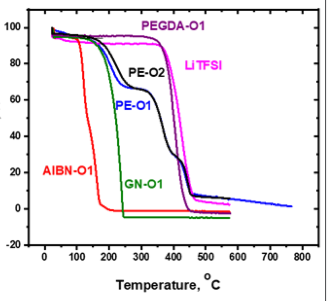


Ionic conductivity (10^{-4} S/cm)				
25°C	45°C	60°C	70°C	80°C
1.4	2.6	5.8	7.9	11

➢ Room temperature ionic conductivity > 10^{-4} S/cm

Thermal property

PE-01 After curing	PEDGA (40wt%) GN (30wt%) LiTFSI (30wt%) AIBN (0.5%)
PE-02 Before curing	PEDGA (40wt%) GN (30wt%) LiTFSI (30wt%) AIBN (0.5%)
PEGDA-01	PEGDA monomer
LiTFSI	LiTFSI powder
GN-01	GN solvent
AIBN01	AIBN powder



➢ TGA test suggests that SPE is thermally stable up to ~200°C.

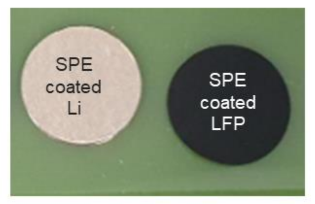
TECHNICAL ACCOMPLISHMENTS AND PROGRESS

SOLID POLYMER ELECTROLYTE IN $LiFePO_4$ CELL

- Li and $LiFePO_4$ electrodes were coated by SPE and put into coin cell for electrochemical testing.
- Good cycle performance was obtained at elevated temperature.

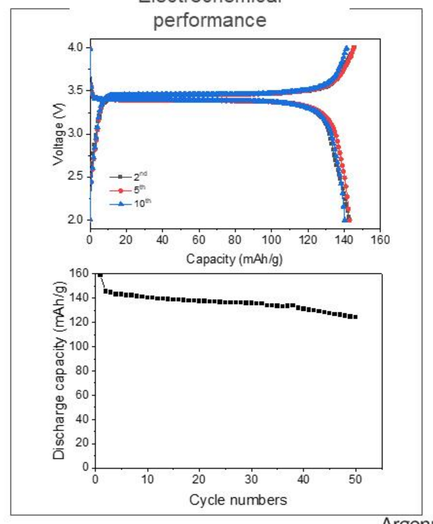
SPE(Wt%)			
PEGDA	LiTFSI	GN	AIBN
40	30	30	0.1

$LiFePO_4$ (Wt%)		
LFP	PVDF	C45
85	10	5



	Anode	Electrolyte	Cathode
Materials	PE coated Li metal (15.6 mm)	-	PE coated LFP electrode (d=16 mm)
Details	Li/SPE/LFP coin cell, 2V-4V @ 45°C, C-rate :0.05C		

Electrochemical performance

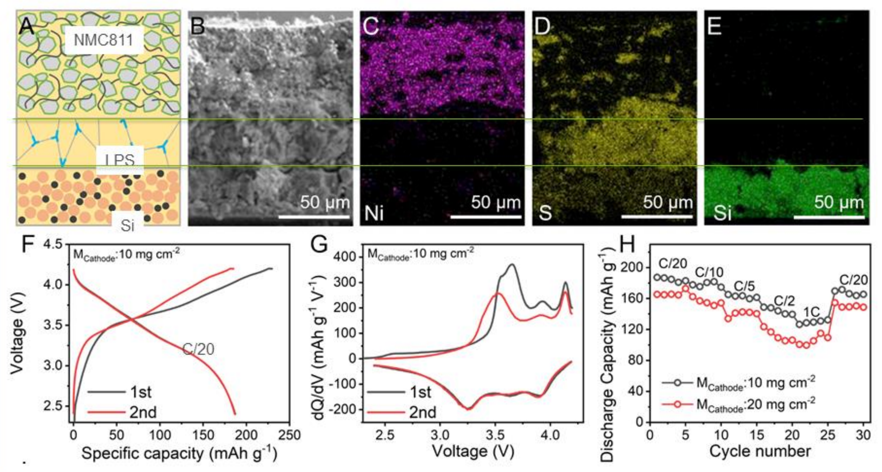


TECHNICAL ACCOMPLISHMENTS AND PROGRESS

Northeastern University, Hongli Zhu

Li_6PS_5Cl ELECTROLYTE IN Si SOLID-STATE CELL

- Li metal as anode in solid state battery faces various challenges, like the unstable interface, low critical current density, and dendrite formation.
- Northeastern University replaced Li with Si as anode and developed a new $Si/Li_6PS_5Cl/NMC811$ all solid-state battery. Argonne demonstrated good electrochemical performance between 2 – 4.2V at room temperature.



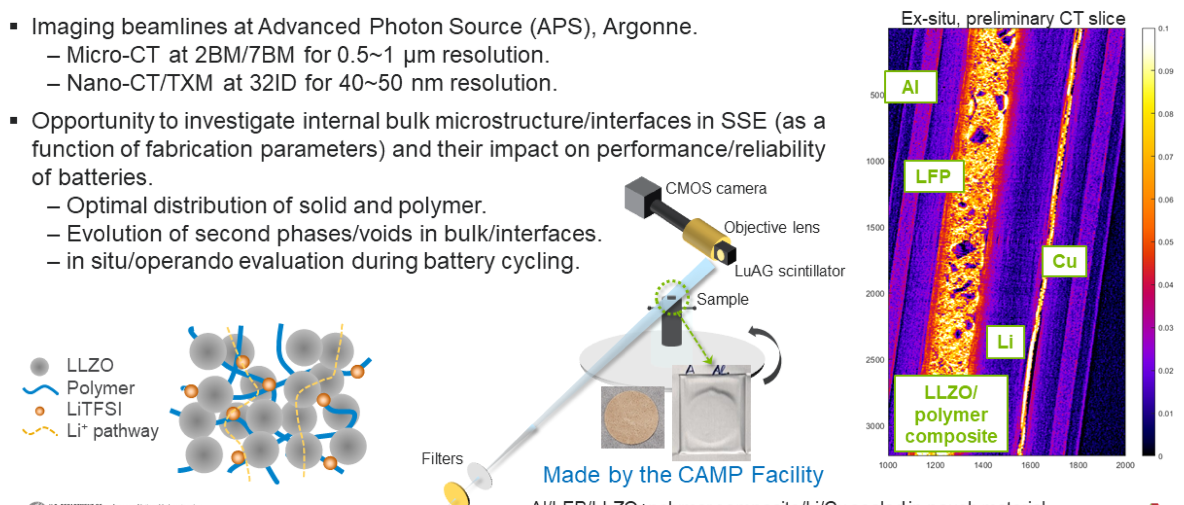
Daxian Cao, Xiao Sun, Yejing Li, Alexander Anderson, Wenquan Lu, Hongli Zhu, Adv. Mater. Accepted, 2022

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

SSE OPTIMIZATION *via* X-RAY IMAGING

Computed tomography (CT) for solid-state electrolyte (SSE) film

- Imaging beamlines at Advanced Photon Source (APS), Argonne.
  - Micro-CT at 2BM/7BM for 0.5~1 μm resolution.
  - Nano-CT/TXM at 32ID for 40~50 nm resolution.
- Opportunity to investigate internal bulk microstructure/interfaces in SSE (as a function of fabrication parameters) and their impact on performance/reliability of batteries.
  - Optimal distribution of solid and polymer.
  - Evolution of second phases/voids in bulk/interfaces.
  - in situ/operando evaluation during battery cycling.



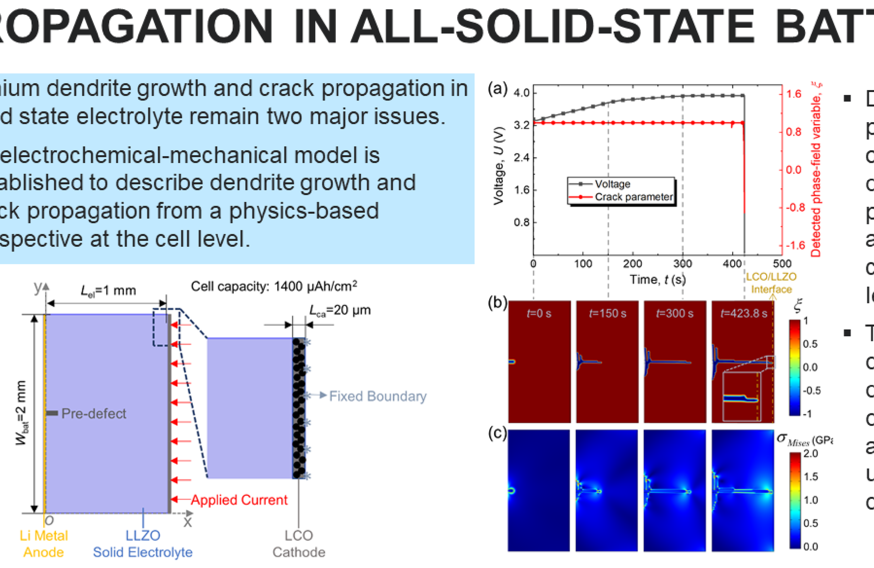
Al/LFP/LLZO+polymer composite/Li/Cu sealed in pouch material.
– LLZO:LITFSI:(PVDF+PTFE) = 70:10:20 of estimated vol%.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

University of North Carolina at Charlotte, Jun Xu

LITHIUM DENDRITE GROWTH AND CRACK PROPAGATION IN ALL-SOLID-STATE BATTERIES

- Lithium dendrite growth and crack propagation in solid state electrolyte remain two major issues.
- An electrochemical-mechanical model is established to describe dendrite growth and crack propagation from a physics-based perspective at the cell level.



- During the charging process, an uneven overpotential η, distribution around the pre-existing defect affects the interfacial chemical reaction, leading to Li plating.
- The high-conductivity dendrite facilitates Li deposition, that is, dendrite growth, and accelerates the uneven overpotential distribution.

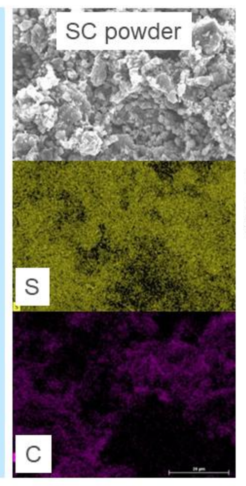
Chunhao Yuan, Wenquan Lu, and Jun Xu, Adv. Energy Mater. 2021, 2101807

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

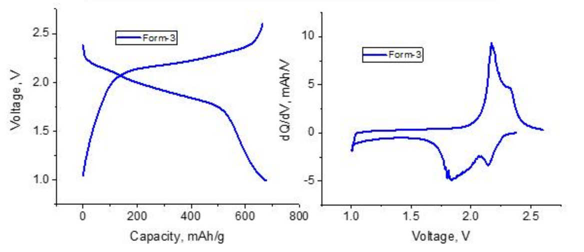
Zeta

ELECTROCHEMICAL STUDY OF SULFUR-CARBON (SC) MATERIAL FROM ZETA ENERGY

- As high energy density and low-cost battery system, the major challenges of Li/S battery are electrically insulating feature of sulfur and high solubility of the polysulfide products.
- Zeta Energy developed a class of novel sulfur-carbon (SC) composite, which demonstrated exceptional cycle performance.
- Slurries & coatings were developed by ANL



- Electrode composition: SC/CB/PAA = 90/5/5
- Electrode loading: 1.3 mAh/cm²
- Formation test 1.0V – 2.6V (C/10) at 30°C



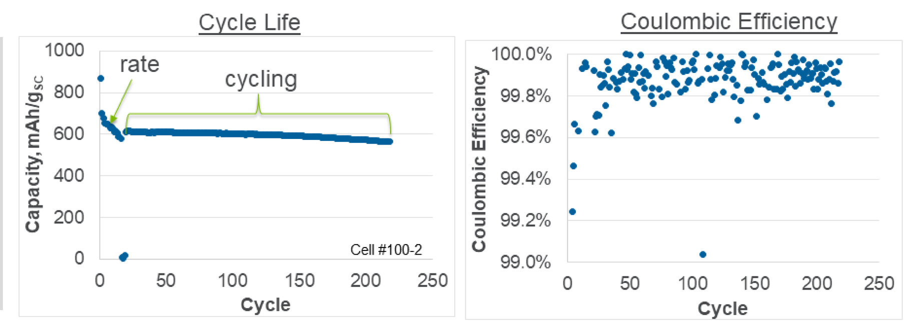
- SEM/EDS suggests that sulfur uniformly distributed within sulfur-carbon (SC) composite.
- Tested sulfur-carbon composite delivered 680 mAh/g at C/10 rate.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

Zeta

ELECTROCHEMICAL STUDY OF SULFUR-CARBON (SC) MATERIAL FROM ZETA ENERGY

Li/SC cell, 1.0 - 2.6V, 30°C
- **Formation Cycles:** C/10, 3 cycles
- **Rate Study Cycles:** C/5, C/3, C/2, 1C, 2C (charge = discharge) 3 cycles/each rate
- **Aging Cycles:** C/5 (charge = discharge)



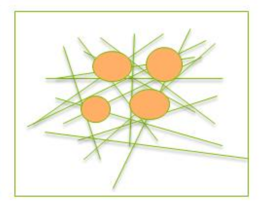
- The Li/SC cell has 89% capacity retention at 1C rate compared to C/5, suggesting good rate performance.
- Coin cell shows excellent cycle life with 92% capacity retention in 200 cycles.

TECHNICAL ACCOMPLISHMENTS AND PROGRESS

CABOT

CARBON NANO-STRUCTURE AS CONDUCTIVE ADDITIVE FOR Si ELECTRODE

- Carbon nanostructure (CNS) matrix can provide good electrical contact for Si electrode by holding the particles together during expansion and contraction.
- SEM shows Si particles embedded in CNS matrix.

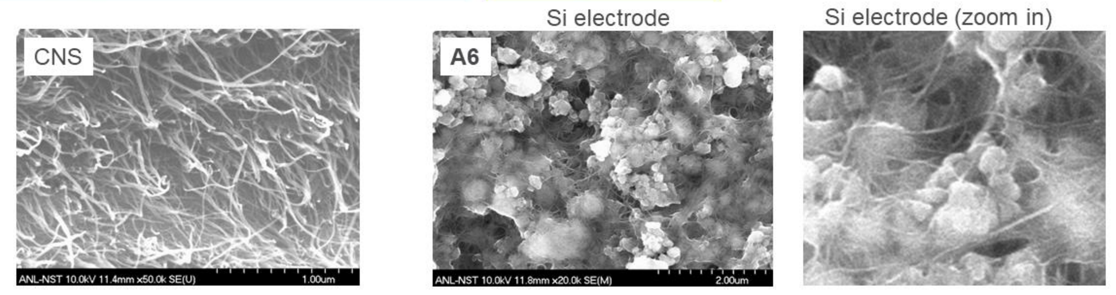


Silicon electrode composition

PESi-A5/A6 (~0.68mg/cm², active)	
Paraclete Energy Si	79%
LiPAA	20%
CNS (Cabot)	1%

Si electrode

Si electrode (zoom in)

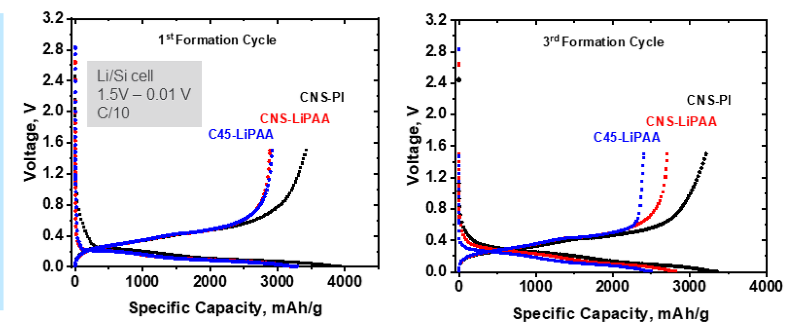


TECHNICAL ACCOMPLISHMENTS AND PROGRESS

CABOT

Si ELECTRODE PERFORMANCE WITH CNS CONDUCTIVE ADDITIVE

- With LiPAA as the binder, CNS sample shows similar 1st cycle capacity and coulombic efficiency as C45, but higher capacity for the 3rd cycle.
- Si electrode with PI binder shows highest capacity for all the formation cycles.



10 % C45, 20% LiPAA

Cycle	charge mAh/g	discharge mAh/g	CE %
1	2866.5	3252.9	88.12
2	2515.4	2925.1	85.99
3	2451.7	2551.5	96.08

1 % CNS, 20% LiPAA

Cycle	charge mAh/g	discharge mAh/g	CE %
1	2886	3263.9	88.4
2	2792	2925.8	95.4
3	2712	2816.1	96.3

1 % CNS, 20% PI

Cycle	charge mAh/g	discharge mAh/g	CE %
1	3429.0	3936.8	87.10
2	3325.5	3423.5	97.13
3	3211.5	3349.0	95.89

RESPONSE TO PREVIOUS YEAR REVIEWERS' COMMENTS

Reviewer's comment: All experimental work is of high quality and results are very encouraging, according to the reviewer. Clear performance/benchmarking targets for each material/component would be helpful. in the slide deck as the performance indicators are only shown at a cell level.
Response: The target/goal for "benchmarking activities" is to search and investigate any existing/emerging battery materials, which can meet DOE's requirements for EV application. Under this effort, we focus on coin cell testing and larger format cell testing is under BAT030 - Electrode Prototyping Activities in ANL's Cell Analysis, Modeling and Prototyping (CAMP) Facility.

Reviewer's comment on BAT030: there is little material assessment being done on "Beyond Li-ion battery" technologies, i.e., either Si-NMC or Li-sulfur (S) technologies."
Response: As part of the CAMP Facility, we started scoping efforts on "Beyond Li-ion battery", such as solid-state electrolyte, and sulfur battery.

Reviewer's comment: This is part of a larger activity (the reviewer was not sure why this should be a separate project) related to the materials benchmarking activities for Cell Analysis, Modeling, and Prototyping (CAMP).
Response: "Benchmarking activities" is an important piece for the CAMP Facility to function effectively.

Reviewer's comment: benchmarking needs to be done on the materials currently used in or rapidly emerging from industry, either in liquid electrolyte or solid electrolyte (SE) systems, but the project does not seem to have established any such connections. Getting access to such materials may be challenging, but efforts should be made in that direction.
Response: We are always open to collaborate with industries and research organizations.

FY21 – FY22 COLLABORATIONS

- The partners and collaborators include
  - National labs: Argonne, INL, LBNL, NREL, ORNL, SLAC, SNL, PNNL
  - Universities: Bingham Young University, IUPUI, Northeastern University, University of Arkansas, University of Louisville, University of Missouri, University of North Carolina at Charlotte, Western Michigan University
  - Industries: Applied Minerals, Blue Ocean and Black Stone, Cabot, Conovate, Jolt Energy Storage Technologies, Koura, Ntherma, Osaka Titanium Corp., OSiAlC, Paraclete Energy, Phillips 66, Superior Graphite Co., Targray, Toda Kogyo, Zeta Energy
- The CAMP Facility is open to work with industries to advance the LIB technologies for EV application.

REMAINING CHALLENGES AND BARRIERS

- High energy active material identification and acquisition remain a challenge.
  - Existing commercial active materials can't meet or exceed DOE/USABC goals.
  - Getting access to advanced active materials is not always successful.
- As a benchmarking activity, the focus of this work is to validate the performance of cell materials (including electrochemical and thermal properties).
  - Research efforts between the validation and research needs to be balanced.

FUTURE RESEARCH

- We will continue the research on solid state electrolyte (SSE), focusing on its conductivity, stable voltage window, and fabrication scalability.
  - Prototype cells using two well studied oxide and sulfide SSE (LLZO, Li_6PS_5Cl) will be fabricated and tested.
- We will continue to acquire and characterize high energy anode/cathode materials from vendors.
  - New active materials, including new binders, electrolytes/additives, and advanced conductive additives, are of interest.
  - Thermal properties of high energy anode/cathode materials will be investigated.
- Continue to work closely with research institutions and industrial suppliers to enable the LIB technology for EV applications.

SUMMARY

- We investigated solid state electrolytes from various aspects:
  - PEGDA solid polymer electrolyte was successfully prepared using thermal curing approach. Good electrochemical performance was obtained using $Li/SPE/LiFePO_4$ cell.
  - $Si/Li_6PS_5Cl/NMC811$ all solid-state battery was fabricated and tested with good cycling performance.
  - We developed an X-ray imaging technique to characterize the solid-state battery.
  - An electrochemical-mechanical model was developed to investigate the lithium dendrite growth and propagation in solid-state electrolyte.
- Sulfur material from Zeta Energy was tested in Li/SC cell and good cycle performance was obtained.
- Carbon Nano Structure materials from Cabot as conductive additive for Si electrode was investigated.

CONTRIBUTORS AND ACKNOWLEDGMENTS

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